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Journal of Organometallic Chemistry 680 (2003) 244–256

Journal of Organometallic Chemistry

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Two-electron homoaromatics with heteroatom bridges

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Received 1 March 2003; accepted 29 April 2003

Dedicated to Professor Fred Hawthorne on the occasion of his 75th birthday

Abstract

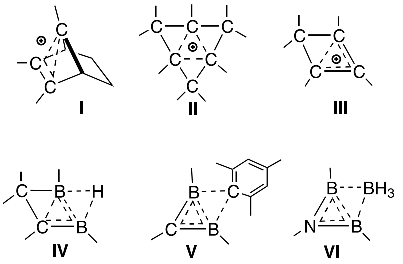
Zwitterionic mono- and bis-homoaromatics **2a–f** and **5a** comprised of positively charged NMe_2, $P(C_6H_5)_2$ or $As(C_6H_5)_2$ bridges and anionic three-center two-electron (3c2e) delocalized boron heterocyclic units, were prepared and characterized by NMR as well as by X-ray structure analyses. The boron chemical shifts of the trishomoaromatic dianion **12a** with an oxygen bridge compare well with those computed ab initio for model **12b**. Analysis of the electronic structure of the bishomoaromatic **5u** and its anionic analog **11u** gives insight into the origin of the trend of increasing effectiveness of BC_2, B_2C and B_3 3c2e bonds: higher electronegativity of carbon vs boron prevents symmetric delocalization in rings with B_2C and especially BC_2 centers.

Keywords: Ab initio computations; Boron heterocycles; Homoaromaticity; Three-center two-electron bonds; Zwitterions

1. Introduction

The concept of homoaromaticity [1] involving three-center two-electron (3c2e) bonding was applied to the bis-homocyclopropenyl cation I [2], the tris-homocyclopropenyl cation II [3], and the (mono-)-homocyclopropenyl cation III [4] (Scheme 1) between 1956 and 1962. Recently, this class of homoaromatics with bridging CH_2 and similar [5] groups bound by the usual two-center two-electron (2c2e) bonds was extended by systems where the bridges involve 3c2e bonds [6]. Hydrogen, sp^2-carbon, or boron [7] atoms (cf. IV–VI), i.e. heteroatoms also can serve as nonclassical [6] homobridges. Heteroatoms as classical homobridges for trishomoaromatic cations have been studied computationally [8].

We now present experimental examples of an unusual class of neutral mono- and bis-homoaromatics with charge compensated heteroatom homobridges bound classically by 2c2e bonds. Such zwitterionic species involving anionic aromatic boron heterocycles arise when the nitrogen, phosphorus or arsene bridging groups bear a positive charge. A dianionic trishomoaromatic with an oxygen homobridge is also described.



Scheme 1.

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doi:10.1016/S0022-328X(03)00396-6

2. Results and discussion

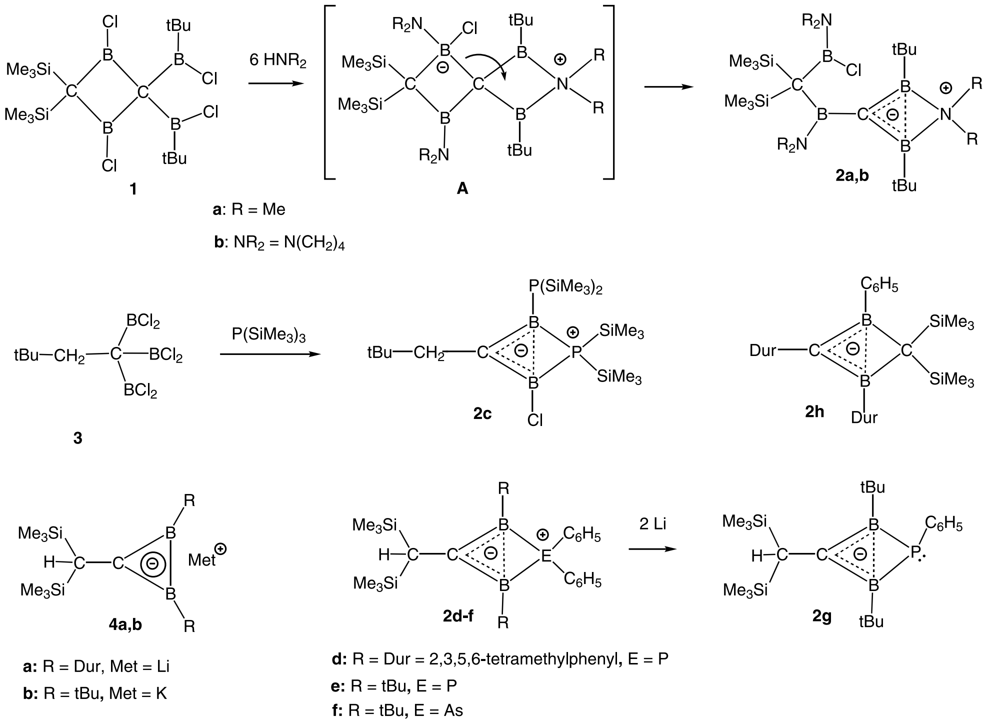
2.1. Monohomoaromatic zwitterions with nitrogen, phosphorus and arsenic homobridges

The zwitterionic 1-azonium-2,4-diboretane-3-ides **2a**,**b** arose unexpectedly during our attempts to replace the chlorine atoms of **1** [9a] by amino substituents, using dimethylamine or pyrrolidine as reagents. A possible mechanism involves intermediate **A**. The driving force for opening the four-membered ring, as shown, is the formation of the 3c2e bond in the observed products **2a**,**b**. Similarly, the zwitterionic 1-phosphonium-2,4-diboretane-3-ide **2c** is obtained from **3** [9b] and $P(SiMe_3)_3$ at 130 °C, while **2d**,**e** and the 1-arsonium-2,4-diboretane-3-ide **2f** are formed at 25 °C when diboriranides **4a**,**b** [10] are reacted with chlorodiphenylphosphane or chlorodiphenylarsane, respectively. Reaction of **2e** with lithium in diethyl ether yields the 1-phospha-2,4-diboretane-3-ide **2g** (Scheme 2).

The structures of **2a**–**d** were confirmed by X-ray structure analyses; those of **2e**–**g** follow from the similarity of the chemical shifts of their skeleton atoms (Table 1) with those of **2d**. For comparison the corresponding chemical shifts of the monohomoaromatic **2h** [11] with a bis(trimethylsilyl)methylene homobridge are included in Table 1.

2.2. A bishomoaromatic zwitterion with an ammonium homobridge

The zwitterionic 1-azonium-2,5-diboracyclopentane-3-ide **5a** is obtained when **6** [12] is reacted with bis(dimethylamino)borane. The structure of **5a** is established by X-ray structure analysis. The ^{11}B-NMR chemical shift of one of its skeleton atoms (−7 ppm) clearly indicates the presence of a pentacoordinate boron atom in solution. The formation of **5a** requires a trimethylsilyl group to migrate from a carbon to a boron atom and a hydrogen atom to migrate from this boron atom to a neighboring carbon. By performing the reaction at low temperature in an NMR tube, we were able to identify two intermediates during this rearrangement. The nonclassical 1,2-diboracyclobutane [13] **7a** is formed at −50 °C. Its structure is deduced from the chemical shifts (12.4 and 35.8) of its skeletal atoms as compared to those (14.8 and 40.9) of **7b**, whose structure is proven by an X-ray analysis. Upon warming to −10 °C, **7a** rearranges into the zwitterionic **8a**, characterized by a ^{13}C-NMR signal at 236 ppm and a boron chemical shift of −5 ppm. Ab initio computations at the GIAO-SCF/6-31G*//MP2(fc)/6-31G* level yield very similar chemical shifts for **8u** ($\delta^{13}C = 227$ and $\delta^{11}B = -7$ ppm). At +10 °C, finally, **8a** transforms into **5a**. This reaction is easily understood as a 1,2-hydride migration from a formally negatively charged boron to a neighboring carbon atom whose partial



Scheme 2.

Table 1
^{11}B and selected ^{13}C-NMR spectroscopic data for **2a**–**h**

	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**
δ^{11}B	37	35	39	44	47	54	38	37
δ^{13}C	151	153	–	179.0	171.2	156.9	140.8	162.9
$J(^{13}C-^{31}P)$	–	–	–	79	82	–	74	–

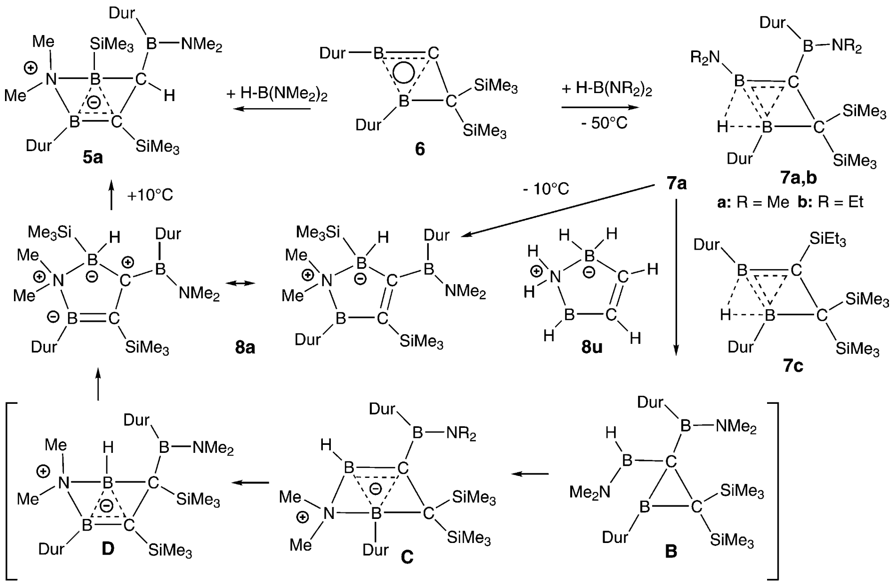
positive charge is indicated by its strong deshielding ($\delta^{13}C = 236$ in **8a**) (Scheme 3).

The rearrangement of **7a** into **8a** can be explained by isomerization of the nonclassical **7a** to the classical **B** (the corresponding opening of unsubstituted **7u**–**Bu** requires only 6.7 kcal mol^{-1} at the MP2/6-31G* level). This is followed by attack of the nitrogen of the hydrogen-bearing boron group at the boron atom of the three-membered ring to yield the bishomoaromatic zwitterion **C**. Migration of a trimethylsilyl group in **C** to the neighboring ring carbon leads to the bishomoaromatic zwitterion **D** which, by further migration of the same silyl group, gives **8a**.

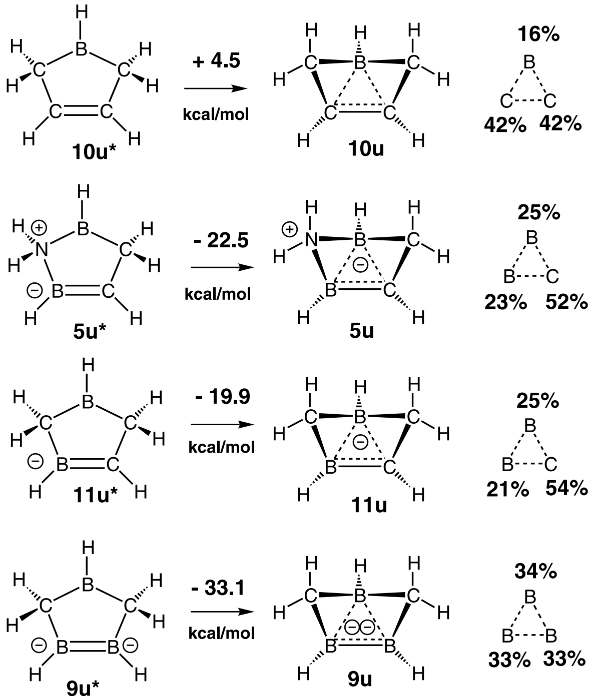
The homoaromatic stabilization energy HSE of **5u**, defined as the energy difference between **5u** and the planar form **5u*** containing a 2c2e B=C double bond, was computed at the MP4/6-311+G**//MP2/6-311+G** level to be −22.5 kcal mol^{-1}. This HSE is between those of **9u** (−33.1) and **10u** (+4.5 kcal mol^{-1}, both at the same level). To elucidate the influence of the positively charged homobridge of **5u** on the HSE, we computed **11u** with an uncharged methylene bridge and **11u***. The HSE of −19.9 kcal mol^{-1} shows that the influence of a positively charged nitrogen homobridge on the degree of homoaromaticity is rather small.

NBO analyses of the electronic structures of **5u** and **11u** reveal why isoelectronic boron heterocycle structures (containing formally a 2c2e π bond and an electron deficient center) are strongly dependent on the number of ring boron atoms: monocyclic derivatives of **10u** have undistorted rings with a C=C bond [14], whereas derivatives of **9u** [15] and **5a** (analogs of **11u**) possess strongly distorted rings due to the 3c2e bonds. Scheme 4 shows the distribution of the cyclically delocalized electrons over the centers of the 3c2e bond as given by NBO analyses.

In **10u**, 84% of the electrons of the 3c2e bond are localized at the carbon atoms, only 16% are found at the boron center. In **9u**, however, the electrons involved in the 3c2e bonding are symmetrically delocalized over the three boron centers. Both **5u** and **11u** are in between: more than 50% of the electrons of the 3c2e bonds are localized at carbon. Evidently, the electronegativities of C and B (2.5 and 2.0, respectively) are decisive. Cyclic delocalization is rather small in **10u**; hence, the gain in energy in forming the 3c2e bond is smaller than the energy required for distortion of the five-membered ring into the geometry characteristic for bishomoaromatic systems. As a consequence, all known monocyclic 1-boracyclopent-3-enes **10** possess structures without 3c2e



Scheme 3.



Scheme 4.

bonds. This is indicated by their ^{11}B NMR chemical shifts (92–96 ppm, characteristic of tricoordinate boron atoms) and is proven by the X-ray analysis of 1-phenyl-3,4-dimethyl-3-borolene [14b]. Only bicyclic systems, which suffer from ring strain in classical conformations, favor bishomoaromatic structures [16]; these have chemical shifts (−7 to −9 ppm) characteristic of pentacoordinate boron atoms.

2.3. A trishomoaromatic dianion with an oxygen homobridge

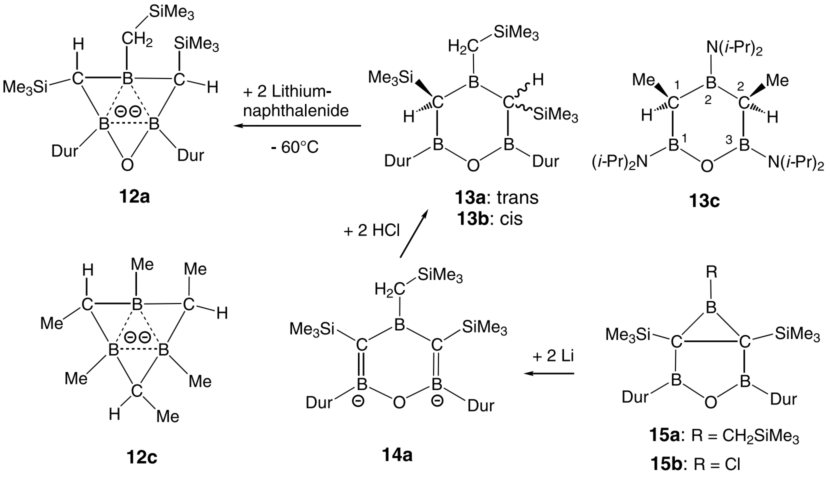
The trishomoaromatic dianion [17] with an oxygen homobridge, **12a**, was generated by reduction of 1-oxa-2,4,6-triboracyclohexane **13a** with excess lithium naphthalenide in THF at −60 °C. Compound **13a** was obtained by protonation (HCl at 25 °C) of the dianion **14a**, which was synthesized by reduction of **15a** (prepared from **15b** [18] and $LiCH_2SiMe_3$) (Scheme 5).

The structures of **14a**$\cdot Li_2 \cdot (Et_2O)_3$ and the stereoisomer **13b** of **13a** were proven by X-ray structure analyses. The structures of **15a** and **13a** follow from the similarity of the chemical shifts of their skeletal atoms with those of **13b** and **15b**. The structure of **15b** also was established by X-ray structure analysis [18]. The *trans*-configuration of **13a** is evident from an AB-multiplet for the protons of the methylene group as a consequence of the chiral centers at C3 and C5.

The ^{11}B-NMR spectrum of dianion **12a**, which could be observed only at temperatures below −40 °C, is shown in Fig. 1. Three sharp signals at −12.1, −15.3 and −23.9 ppm as compared to $\delta^{11}B = -29.2$ ppm for **12c**, the trishomoaromatic structure of which is established by an X-ray analysis [17], strongly hint at similar structures for **12a** and **12c**. Deshielding of the boron atoms of **12a** bound to oxygen is to be expected as an electronegativity effect. Additional support for the trishomoaromatic nature of **12a** was obtained by ab initio computations of the chemical shifts of model **12b**. The results obtained at the GIAO-SCF/6-31+G*//B3LYP/6-31+G* and GIAO-B3LYP/6-31+G*//B3LYP/6-31+G* levels shown in Fig. 2 are in convincing agreement with the experimental data.

3. Structures

Compounds **2a**–**d** (Figs. 3–5) are the first homoaromatic ring systems with heteroatoms bridging two boron centers. All show folded four-membered rings with B1–C1–B2–N1 or B1–C1–B2–P torsion angles between 26.2(2) and 19.2(3)° (see Table 2). The C1–B1 and C1–



Scheme 5.

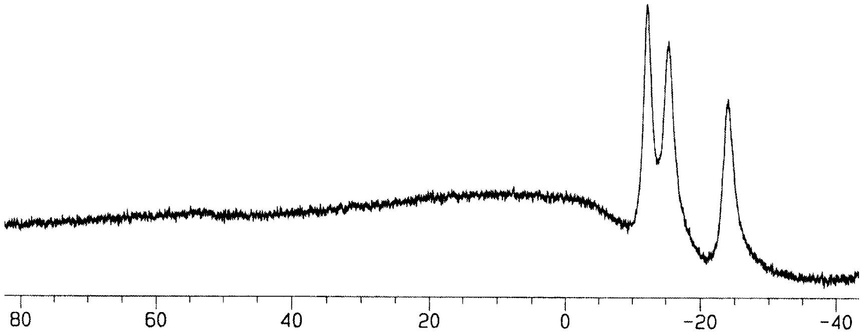
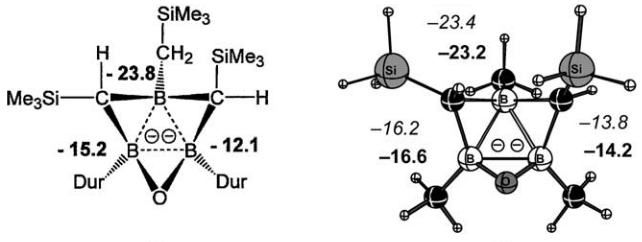


Fig. 1. ^{11}B-NMR spectrum of **12a** in THF at −60 °C.



12a **12b**

Fig. 2. Experimental and computed (GIAO-SCF/6-31G*//B3LYP/6-31+G* in italics and GIAO-B3LYP/6-31+G*//B3LYP/6-31+G*) ^{11}B chemical shifts of **12a** and model **12b**, respectively.

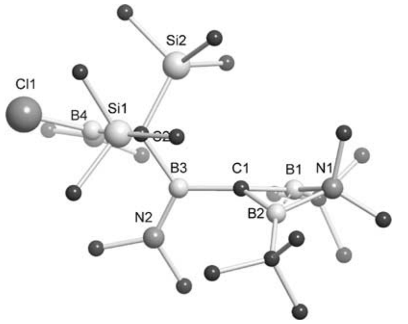


Fig. 3. Molecular structure of **2a** in the crystal, H-atoms omitted for clarity; selected bond lengths (pm) and angles (°) completing Table 2. B3–N2 142.3(2), C1–B2–N1 98.2(1), B1–C1–B2–B3 25.7(2).

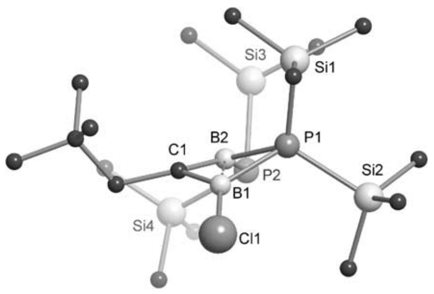


Fig. 4. Molecular structure of **2c** in the crystal, H-atoms omitted for clarity; selected bond lengths (pm) and angles (°) completing Table 2. B2–P2 192.4(3), B1–Cl1 179.3(3), P1–Si1/Si2 226.3(1)/226.8(1), P2–Si3/Si4 224.5(1)/224.7(1), C1–B2–P1 96.7(2), C1–C2/B1–C1–B2 84.2(2).

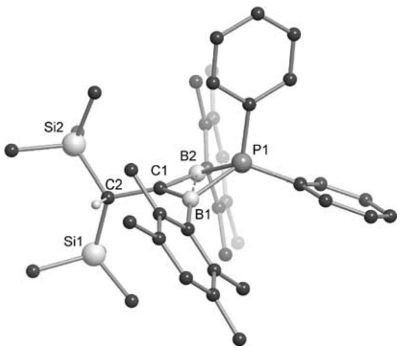


Fig. 5. Molecular structure of **2d**·Et$_2$O in the crystal, H-atoms Et$_2$O omitted for clarity; selected bond lengths (pm) and angles (°) completing Table 2. B1–C10 158.1(5), B2–C20 158.9(5), C2–Si < 189.1(4) >, P1–C < 181.0(3) >, C1–B2–P1 92.3(2), C30–P1–C36 104.1(2) (average over both molecules, labels of molecule 1).

B2 bond lengths are short due to additional bonding by the 3c2e bond which also explains the short transannular B1···B2 distance in **2a** (as in **2h** [11]). The longer B1···B2 distances in **2c**,**d** are the consequence of inherently longer bonds to phosphorus. The small angles at N1 and P1 are characteristic for homobridges (compare this feature in **2h**). The B1 and B2 distances to N1 and P1 indicate single bonds to the bridging atoms. NBO analyses of the prototype molecules **2uN** and **2uP** (type **2d**,**e** molecules without any substituents) show the presence of 3c2e bonds between C1, B1 and B2, i.e. both are homoaromatic systems.

The crystal structure of **5a** (Fig. 6) shows a strongly distorted five-membered ring with short transannular B2···C1 (182.8(2) pm) and B2···B1 (198.2(3) pm) distances, small angles at the homobridges (B1–N1–B2: 77.6(1)°, C1–C2–B2: 71.3(1)°), and an interplanar angle of 84.6(8)° between the best plane through N1–B1–C1–C2 and the plane N1–B2–C2. MP2/6-31+G* computations for **5u** gave transannular distances of 174.3 and 187.8 pm, angles at the homobridges of 73.4 and 69.0° and an interplanar angle of 85.1°. For planar **5u*** the corresponding data are 242.4 and 250.7 pm and 104.6 and 104.3°. The deformations in **5u** (and **5a**) as compared to **5u*** are characteristic of bishomoaromatic five-membered rings [19]. Considerably longer transan-

Table 2
Selected bond lengths (pm), and angles (°) for **2a**,**c**,**d** (experimental) and **2uN**, **2uP** (computed at the B3LYP/6-311+G** level)

	2a	**2c**	**2d**	**2uP**	**2uN**
B1–C1	148.9(2)	146.0(4)	149.9(5)	148.0	146.2
B2–C1	148.7(2)	148.3(3)	150.4(5)	148.0	146.2
B1–X	159.6(2) [a]	192.7(3) [b]	193.3(4) [b]	195.9 [b]	158.3 [a]
B2–X	159.0(2) [a]	200.9(3) [b]	193.3(4) [b]	195.9 [b]	158.3 [a]
C1–B3(C2)	156.4(2)	150.3(3)	153.4(4)	–	–
B1···B2	189.5(2)	209.5(4)	226.4(5)	226.6	193.1
B1–C1–B2	78.8(1)	90.8(2)	97.9(3)	99.9	82.6
B1–X–B2	73.0(1) [a]	64.3(1) [b]	71.7(2) [b]	70.7 [b]	74.6 [a]
C1–B1–X	98.3(1) [a]	101.1(2) [b]	92.5(2) [b]		
B1–C1–B2–X	26.2(2) [a]	21.6(2) [b]	19.2(3) [b]		
C1–B1–B2–X	147.1(2) [a]	153.8(2) [b]	154.9(3) [b]	154.6 [b]	151.8 [a]

[a] X = N1.
[b] X = P1.

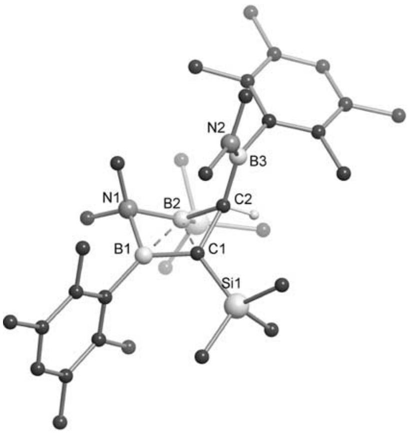


Fig. 6. Structure of **5a** in the crystal, most H-atoms omitted for clarity; selected bond lengths (pm) and angles (°): C1–B1 147.9(3), C1–B2 182.8(2), C1–C2 155.6(2), C1–Si1 186.6(2), B1–N1 156.9(2), B1···B2 198.2(3), B1–C10 158.6(3), N1–B2 159.6(3), B2–C2 158.0(3), B2–Si2 202.3(2), C2–B3 157.5(3), B3–N2 140.2(2), B3–C20 160.3(3); B1–C1–B2 72.8(1), C1–B1–N1 106.9(2), B1–N1–B2 77.6(1), N1–B2–C1 91.1(1), C2–C1–B2 55.0(1), C1–B2–C2 53.7(1), C1–C2–B2 71.3(1); B2–C1–B1–N1 −26.3(1), C1–B1–N1–B2 29.8(2), C1–B1–B2–N1 −147.4(2), B1–C1–B2–C2 143.1(2), C1–B2–C2–B3 −133.6(2).

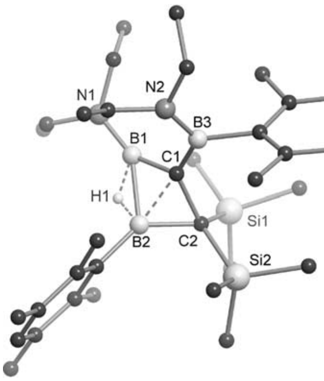


Fig. 7. Structure of $\mathbf{7b}\cdot 0.5C_6H_{14}$ in the crystal, most H-atoms omitted for clarity; selected bond lengths (pm) and angles (°): C1–B1 150.8(2), C1–B2 167.4(2), C1–B3 158.6(2), C1–C2 159.6(2), B1–B2 181.6(3), B1–N1 138.6(2), B1–H1 131(2), B2–H1 136(2), B2–C2 160.3(3), B2–C10 159.9(3), C2–Si1/Si2 188.9(2)/188.5(2), B3–N2 140.4(3); C1–B1–B2 59.6(1), B1–C1–C2 106.1(1), B1–C1–B2 69.4(1), B1–B2–C2 92.9(1), B1–B2–C1 51.0(1), C2–C1–B2 58.7(1), C2–B2–C1 58.2(1), C1–C2–B2 63.1(1), C1–B3–N2 123.2(2); B1–C1–B2–C2 125.3(1), C1–B1–C2–B2 103.9(2), C1–B1–B2–H1 −153(1), B1–C1–B3–N2 37.0(3).

nular distances in **5a** as compared to **5u** can be explained by the steric repulsion of the three large substituents at the centers of the 3c2e bond in **5a**.

Compound **7b** (Fig. 7) is the first nonclassical 1,2-diboretane [13] with an amino substituent at only *one* of the skeleton boron atoms. 1,2-Diboracyclobutanes with amino substituents at *both* boron atoms, like 1,2-diamino-1,2-diboracyclopentanes [20], have classical structures [21]. The transannular C1···B2 distance of **7b**, shorter (167.4(2) pm) than in **7c** [13] (172.3(3) pm) with two duryl substituents at the ring boron atoms, indicates a rather strong 3c2e bond. B1–C1 (150.8(2) pm in **7b**) is slightly longer than in **7c** (147.2(3) pm). Surprisingly, the B1–N1 distance (138.6(2) pm, compare the internal standard 140.4(3) pm for B3–N2) is characteristic of partial B–N double bonds [22]. Thus B1 is involved in the 3c2e B1, C1, B2 bond (as well as the B1, H, B2 bond) despite of its partial double bond to N1. The sum of the angles around N1 is 360.0°.

The conformation of **13b** is distinctly different from that of **13c** [23] with donor substituents at all boron atoms and methyl instead of trimethylsilyl groups at the ring carbon atoms (Fig. 8). While **13c** is strongly folded along the B1–B2 axis, thus containing an almost planar five-membered ring, **13b** is a flat chair: the C1, B1, B2, O1 plane (maximum deviation from the best plane 0.8 pm) has angles of 24.3(2) and 10.5(2)°, respectively, with the B1, C2, B2 and C1, O, B3 planes. All ring C–B bonds in **13b** are shorter than the corresponding bonds in **13c**. The bond distances of the silicon atoms bound to the ring are distinctly longer than in the exocyclic H_2C–Si bond. All these findings can be explained by

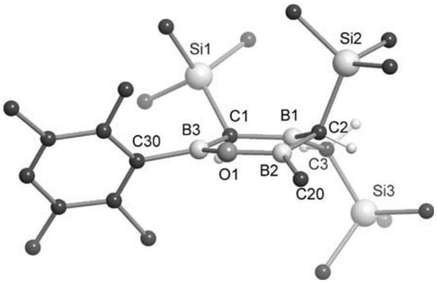


Fig. 8. Structure of **13b** in the crystal, duryl residue at B2 and most H-atoms omitted for clarity; selected bond lengths (pm) and angles (°): B1–C1 157.5(3), B1–C2 158.2(2), B1–C3 157.6(2), C1–B3 157.3(2), C1–Si1 191.6(2), B3–O1 138.7(2), B3–C30 1.583(3), O1–B2 138.6(2), B2–C2 156.0(2), B2–C20 159.3(2), C2–Si2 190.9(4), C3–Si3 187.7(8); C1–B1–C2 118.0(1), B1–C1–B3 115.9(1), B3–O1–B2 127.1(1), O1–B2–C2 120.2(1), B2–C2–B1 112.6(1); B3–C1–B1–C2 −21.6(2), B1–C1···O1–B3 −169.0(2), C1–B1···B2–C2 −155.2(2).

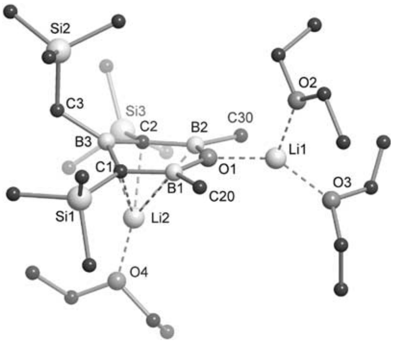


Fig. 9. Structure of **14a**·Li_2·$(Et_2O)_3$ in the crystal, H-atoms and duryl residues omitted for clarity; selected bond lengths (pm) and angles (°): B1–O1 144.1(8), B1–C1 150(1), B1–C20 159.5(8), C1–B3 155.1(8), C1–Si1 185.6(6), B3–C2 155.7(9), B3–C3 161.0(8), C2–B2 151.4(9), C2–Si3 184.6(6), B2–O1 146.2(7), B2–C30 158(1), Li1–O1 196(1), Li1–O2 196(1), Li1–O3 195(1), Li2–O4 193(1), Li2···C1 222(1), Li2···B3 230(1), Li2···C2 221(1), Li2···B1 265(1), Li2···B2 266(1), Li2···O1 285(1); O1–B1–C1 121.4(5), B1–C1–B3 114.0(5), C1–B3–C2 116.6(5), B3–C2–B2 117.1(5), C2–B2–O1 117.4(6); B2–O1–B1–C1 −5.0(8), O1–B1–C1–B3 −15.9(8), B1–C1–B3–C2 34.2(7), B1–C1···C2–B3 −149.1(7), B3–C2–B2–O1 12.5(8).

hyperconjugation of ring –C–Si bonds with two neighboring boron atoms.

The salt **14a**·Li_2·$(Et_2O)_3$ is a contact triple ion (Fig. 9). Li1 is coordinated to two ether molecules and to O1, Li2 to the remaining atoms of the central ring and to one Et_2O. While the Li2–C1 (222(1) pm), Li2–C2 (221(1) pm) and Li2–B3 (230(1) pm) distances are comparable to those in aromatic diboratabenzene dianions [16b,24], Li2–B1 and Li2–B2 (265(1) and 266(1) pm) are considerably longer. C1, B1, O1, B2, C2 of the central ring lie almost in one plane, but the folding along the C1–C2 axis is 30.1(7)°. This reduces steric hindrance between the substituent at B3 and the trimethylsilyl substituents at C1 and C2.

Computations of unsubstituted **14u** without counter ions lead to a planar six-membered ring. Despite being isoelectronic with the pyrylium cation, **14u** is not aromatic as indicated by its NICS value of 0.8 at the center of the ring. This is reminiscent of the findings for borazine and boroxine [25]. Differences in electronegativity of the centers of cyclic delocalization are responsible for the deviation from the Hückel rule. Differences in electronegativity also are the reason for the non-homoaromatic nature of **10u** despite being isoelectronic with the strongly homoaromatic **5u**, **9u** and **11u**. As is to be expected: aromaticity and homoaromaticity are governed by the same principles!

4. Conclusions

The properties of two-electron homoaromatics with heteroatom bridges are similar to those of the corresponding species with methylene bridges. The realization of the first bishomoaromatic with a delocalized bond between two boron and one carbon center (B_2C) completes the 3c2e boron–carbon series. The other members of this set have C_3, BC_2, and B_3 centers, although some of the known examples involve bicyclic systems. Computations on prototype models show that the homoaromatic stabilization energies decrease with the number of carbon centers due to the higher electronegativity of carbon than boron. The high electronegativity of oxygen precludes effective cyclic electron delocalization (aromaticity) in 1-oxa-2,4,6-triboracyclohexane-diide, the isoster of the aromatic pyrylium cation.

5. Experimental

5.1. General

Reactions were carried out under dry argon or nitrogen, using standard Schlenk techniques. Solvents were dried, distilled, and saturated with nitrogen. Glassware was dried with a heat-gun in high vacuum. ^1H, ^{13}C-NMR: Bruker DRX 200 spectrometer and Bruker AC 500, ^{11}B-NMR: Bruker DRX 200 spectrometer, NMR references are $(CH_3)_4Si$ and BF_3·Et_2O. Mass spectra were obtained with a ZAB-2F VH Micromass CTD spectrometer, high resolution mass spectra with a Joel MS Station JMS-700 spectrometer. Melting points (uncorrected) were measured with a Büchi apparatus using capillaries, which were filled under argon or nitrogen and sealed.

*5.2. 3-{Dimethylamino-[bis(trimethylsilyl)(dimethylamino-chloro-boryl)methyl]boryl}-1-bis(trimethylsilyl)azonium-2,4-bis(t-butyl)-2,4-diboretane-3-ide (**2a**)*

To a solution of 200 mg (0.43 mmol) of **1** in 10 ml of hexane 0.8 ml of dimethylamine were added at −30 °C. The mixture was allowed to warm to room temperature (r.t.) and was refluxed for 3 h. After filtration of insoluble salts the solvent was reduced and the solution cooled to −80 °C to yield colourless crystals, m.p.: 145–147 °C (dec.). Yield: 144 mg (68 %) **2a**. ^{1}H-NMR (200 MHz, [d_8]-toluene, 313 K) $\delta = 0.41$ (s, 18H, $SiMe_3$), 1.04 (s, 18H, CMe_3, 2.48 (s, 3H, NMe), 2.58 (s, 3H, NMe), 2.70 (s, 6H, NMe), 2.73 (s, 3H, NMe), 2.90 (s, 3H, NMe), ^{11}B-NMR (64 MHz, $CDCl_3$) $\delta = 43$, 37 (1:3), ^{13}C-NMR (50 MHz, $CDCl_3$) $\delta = 2.0$ (q, $SiMe_3$), 4.9 (q, $SiMe_3$), 6.8 (q, $SiMe_3$), 7.3 (q, $SiMe_3$), 8 (br. s, CB_3), 22 (br. s, $\underline{C}Me_3$), 30.0 (s, CMe_3), 30.6 (s, CMe_3), 30.8 (s, CMe_3), 32.2 (s, CMe_3), 37 (br. s, CB_2), 41.3 (q, NMe), 42.7 (q, NMe), 44.4 (q, Me), 44.6 (q, Me), 45.0 (q, NMe_2), 58.1 (q, NMe_2), CI-MS *m/z* (%): 495 (23) [M^+], 460 (100) [M^+−Cl], HR-MS (EI): *m/z* 438.3225 [$M^+ - CCH_3$], Calc. $^{12}C_{18}$ $^{1}H_{45}$ $^{11}B_4$ $^{35}Cl_1$ $^{14}N_3$ $^{28}Si_2$: 438.3213, ($\Delta =$ 1.2mmu).

*5.3. 3-{Pyrrolidino-[bis(trimethylsilyl)(pyrrolidino-chloro-boryl)methyl]boryl}-1-bis(trimethylsilyl)azonium-2,4-bis(t-butyl)-2,4-diboretane-3-ide (**2b**)*

Tree hundred and three milligram (4.26 mmol) of pyrrolidine were added to a solution of 250 mg (0.53 mmol) of **1** in 15 ml of hexane at −50 °C. The mixture was allowed to warm to r.t. and then was refluxed over night. After filtration of insoluble salts the solvent and volatile compounds were removed in vacuum and an orange solid was crystallized from toluene. Yield: 210 mg (58 %), **2b**. ^{1}H-NMR (200 MHz, [d_8]-toluene) $\delta =$ 0.23 (s, $SiMe_3$), 0.29 (s, $SiMe_3$), 0.37 (s, $SiMe_3$), 0.59 (s, $SiMe_3$), 1.09 (s, CMe_3), 1.10 (s, CMe_3), 1.19 (s, CMe_3), 1.56 (m, NCH_2), 2.96–3.74 (m, NCH_2CH_2), ^{11}B-NMR (64 MHz, C_6D_6) $\delta = 44$, 35 (3:1), ^{13}C-NMR (50 MHz, [d_8]-toluene) $\delta = 3.7$ (q, $SiMe_3$), 5.1 (q, $SiMe_3$), 6.5 (q, $SiMe_3$), 6.6 (q, $SiMe_3$), 24.2 (t, NCH_2), 24.7 (t, NCH_2), 25.2 (t, NCH_2), 25.7 (t, NCH_2), 25.8 (t, NCH_2), 26.2 (t, NCH_2), 26.9 (t, NCH_2), 27.1 (t, NCH_2), 27.2 (t, NCH_2), 28.0 (t, NCH_2), 29.7 (q, CMe_3), 30.4 (q, CMe_3), 31.1 (q, CMe_3), 48.9 (t, NCH_2CH_2), 49.8 (t, NCH_2CH_2), 50.1 (t, NCH_2CH_2), 50.3 (t, NCH_2CH_2), 50.4 (t, NCH_2CH_2), 50.9 (t, NCH_2CH_2), 51.1 (t, NCH_2CH_2), 52.4 (t, NCH_2CH_2), 68.5 (t, NCH_2CH_2), CB not observed,-CI-MS *m/z* (%): 574 (1) [M^+],-HR-MS (EI): *m/z* 516.3702 [$M^+ - C(CH_3)_3$], Calc. $^{12}C_{24}$ $^{1}H_{51}$ $^{11}B_4$ $^{35}Cl_1$ $^{14}N_3$ $^{28}Si_2$: 516.3722 ($\Delta =$ 2.0mmu).

*5.4. 3-(2,2-Dimethylpropyl)-1-bis(trimethylsilyl)phosphonium-2-chloro-4-bis(trimethylsilyl)phosphyl-2,4-diboretane-3-ide (**2c**)*

A mixture of 1.32 g (4.02 mmol) of **3** and 4.20 g (16.76 mmol) of $P(SiMe_3)_3$ was heated for 2.5 h at 130 °C and then the volatiles were removed in vacuum. The red–brown residue was distilled at 90–100 °C/0.02 mbar to give an orange oil, containing **2c** and other products. A solution of the orange oil in CH_2Cl_2 was kept for several days at 4 °C to give crystals of yellow **2c** (70 mg, 4%) and traces of colourless $[(Me_3Si)_2PBCl_2]_2$ [26]. ^{1}H-NMR (200 MHz, [d_8]-toluene, 313 K), $\delta = 0.26$ (s, 9H, $SiMe_3$), 0.29 (s, 9H, $SiMe_3$), 0.38 (s, 9H, $SiMe_3$), 0.42 (s, 9H, $SiMe_3$), 0.84 (s, 9H, CMe_3), 2.02 (s, 2H, CH_2); ^{11}B-NMR $\delta = 39$, EI-MS: (*m/z*, %), 494 (M^+, 1), 458 (M^+−HCl, <1), 437 ($M^+ - C_4H_9$, 3), 421 ($M^+ - SiMe_3$, 1), 365 ($M^+ - C_4H_8$, −SiMe, 1), 73 ($SiMe_3^+$, 100), 57 ($C_4H_9^+$, 6). HR-MS(EI): *m/z* 494.2094 M^+, Calc. $^{12}C_{18}$ $^{1}H_{47}$ $^{11}B_2$ ^{35}Cl $^{31}P^{28}Si_4$: 494.2104, ($\Delta = 1.0$ mmu).

*5.5. 2,4-Bis(2′,3′,5′,6′-tetramethylphenyl)-3-bis(trimethylsilyl)methyl-1,1-diphenyl-1-phosphonium-2,4-diboretane-3-ide (**2d**)*

A solution of 0.47 g (2.14 mmol) chlorodiphenylphosphane in 10 ml pentane was added to a cooled (−68 °C) suspension of 1.0 g (2.14 mmol) of the diboriranide **4a** in 30 ml Et_2O. After warming to r.t. and 2 h stirring, all volatiles were removed, the residue digested with 40 ml of pentane, the salt separated by a D4 revised frit and washed two times with 10 ml pentane. Removal of the solvent in vacuum yielded light yellow **2d** in NMR-spectroscopic purity. After about 2 weeks in Et_2O at −35 °C colourless crystals, m.p. 181–182, were obtained. Yield: 680 mg (53%) **2d**. ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 0.03$ (s, 18H, $Si(CH_3)_3$), 2.10 (s, 1H, CH), 2.17, 2.27 (each s, each 12H, *o*- and *m*-CH_3), 7.02 (s, 2H, *p*-Dur), 7.33–7.36, 7.40–7.43, 7.51–7.57 (m, altogether 10H, H–Ph), ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 1.4$ (q, 6C, $Si(CH_3)_3$), 19.8, 21.4 (each q, each 4C, *o*- and *m*-CH_3), 30.1 (d, 1C, HCSi), 128.3 (d, 4C, $J(^{13}C-^{31}P) = 10$ Hz, *m*-Ph), 129.6 (d, 2C, $J(^{13}C-^{31}P) = 7$ Hz, *p*-Ph), 130.6 (s, 2C, *p*-C of Dur), 133.0 (d, 2C, $J(^{13}C-^{31}P) = 42$ Hz, *i*-C of Ph), 133.1 (d, 4C, $J(^{13}C-^{31}P) = 9$ Hz, *o*-C of Ph), 134.4 (d, 2C, $J(^{13}C-^{31}P) = 10$ Hz, *o*-C of Dur), 141.0 (br., 2C, *i*-C of Dur), ^{13}C {^{11}B(44 ppm)}-NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 179.0$ (d, 1C, $J(^{13}C-^{31}P) = 79$ Hz, CB_2), ^{11}B-NMR (96 MHz, $CDCl_3$, 25 °C): $\delta = 44$.

*5.6. 3-Bis(trimethylsilyl)methyl-2,4-di-t-butyl-1,1-diphenyl-1-phosphonium-2,4-diboretane-3-ide (**2e**)*

In analogy to the procedure for **2d**, from 1.34 g (6.06 mmol) of chlordiphenylphosphane and 2.0 g (6.06

mmol) of **4b**, colourless crystals, m.p. 116 °C, of **2e** were obtained from pentane at −30 °C. Yield: 2.15 g (72%). **2e**: ^{1}H-NMR ($CDCl_3$, 25 °C): $\delta = 0.07$ (s, 18H, $Si(CH_3)_3$), 1.07, 1.13 (each s, each 9H, $C(CH_3)_3$), 2.38 (s, 1H, $HCSi_2$, $^{1}J(^{1}H-^{31}P) = 2.7$ Hz), 7.34–7.66 (m, 10H, H–Ph), ^{13}C-NMR (100 MHz, $CDCl_3$, −40 °C): $\delta = 1.0$ (q, 6C, $Si(CH_3)_3$), 23.4 (br. s, 1C, $C(CH_3)_3$, $^{2}J(^{13}C-^{31}P) = 8.5$ Hz), 24.1 (br. s, 1C, $C(CH_3)_3$, $^{2}J(^{13}C-^{31}P) = 12.2$ Hz), 28.3 (d, 1C, $HCSi_2$, $^{3}J(^{13}C-^{31}P) = 46.5$ Hz), 30.7 (q, 3C, $C(CH_3)_3$, $^{3}J(^{13}C-^{31}P) = 4.9$ Hz), 31.0 (q, 3C, $C(CH_3)_3$, $^{3}J(^{13}C-^{31}P) = 5.2$ Hz), 128.3 (d, 4C, *m*-C, $^{3}J(^{13}C-^{31}P) = 10.5$ Hz), 129.1 (d, 2C, *p*-C), 131.9 (s, 2C, *i*-C, $^{1}J(^{13}C-^{31}P) = 49.6$ Hz), 133.4 (d, 4C, *o*-C, $^{2}J(^{13}C-^{31}P) = 10.4$ Hz), 171.2 (br., s, 1C, CB_2, $^{2}J(^{13}C-^{31}P) = 82.1$ Hz), ^{11}B-NMR ($CDCl_3$, 25 °C): $\delta = 47$, ^{31}P-NMR ($CDCl_3$, 25 °C): $\delta = -39.6$.

5.7. 3-Bis(trimethylsilyl)methyl-2,4-di-t-butyl-1,1-diphenyl-1-arsonium-2,4-diboretane-3-ide (2f)

Analogously to the procedure for **2e**, employing 1.33 g (5.0 mmol) chlorodiphenylarsane and 1.65g (5.0 mmol) **4b** gave light yellow crystals, m.p. 95 °C (dec.) of **2f** from 10 ml pentane. Yield: 1.77 g (66.1%). **2f**: ^{1}H-NMR ($CDCl_3$, 25 °C): $\delta = 0.07$ (s, 18H, $Si(CH_3)_3$), 1.07, 1.10 (each s, each 9H, $C(CH_3)_3$), 2.16 (s, 1H, $HCSi_2$), 7.33–7.56 (m, 10H, H–Ph),^{13}C-NMR (100 MHz, $CDCl_3$, −35 °C): $\delta = 0.8$ (q, 6C, $Si(CH_3)_3$), 24.1, 24.7 (each s, each 1C, $C(CH_3)_3$), 26.1 (d, 1C, $HCSi_2$, $^{1}J(^{13}C-^{1}H) = 102.4$ Hz), 30.4 (q, 6C, $C(CH_3)_3$, 128.6 (d, 2C, *p*-C), 128.7 (d, 4C, *m*-C), 133.0 (d, 4C, *o*-C), 134.0 (s, 2C, *i*-C), 156.9 (br., s, 1C, CB_2), ^{11}B-NMR ($CDCl_3$, 25 °C): $\delta = 54$.

5.8. 3-Bis(trimethylsilyl)methyl-2,4-di-t-butyl-1-phenyl-1-phospha-2,4-diboretane-3-ide (2g)

0.80 g (1.63 mmol) of compound **2e** dissolved in 8 ml THF were added to a suspension of 0.12 g (17.3 mmol) Li-powder in 15 ml of THF. The reaction mixture slowly turned dark red. After 4 h, excess Li metal was separated by a reversed frit and the filtrate evaporated in vacuum. Orange solid, yield 0.61g (87.4%). **2g**: ^{1}H-NMR ([d_{10}]-DME, 25 °C): $\delta = -0.15$, 0.10 (each s, each 9H, $Si(CH_3)_3$), 0.83, 0.90 (each s, each 9H, $C(CH_3)_3$), 2.11 (s, 1H, $HCSi_2$, $^{1}J(^{1}H-^{13}C) = 104.2$ Hz), 6.72, 7.30 (each m, altogether 5H, H–Ph), ^{13}C-NMR (([d_{10}]-DME, 25 °C): $\delta = 1.2$, 2.8 (each q, each 3C, $Si(CH_3)_3$), 25.3 (dd, 1C, $HCSi_2$, $^{3}J(^{13}C-^{31}P) = 17.8$ Hz, $^{1}J(^{13}C-^{1}H) = 104.1$ Hz), 32.9, 33.9 (each dq, each 3C, $C(CH_3)_3$, $^{3}J(^{13}C-^{31}P) = 2.7$ Hz), 123.1 (dd, 1C, *p*-C, $^{1}J(^{13}C-^{1}H) = 156.7$ Hz), 125.8 (dd, 2C, *m*-C, $^{3}J(^{13}C-^{31}P) = 3.8$ Hz, $^{1}J(^{13}C-^{1}H) = 157.4$ Hz), 136.3 (dd, 2C, *o*-C, $^{2}J(^{13}C-^{31}P) = 14.9$ Hz, $^{1}J(^{13}C-^{1}H)$, 156.2 Hz), 155.4 (d, 1C, *i*-C, $^{1}J(^{13}C-^{31}P) = 64.8$ Hz), ^{11}B-NMR ([d_{10}]-DME, 25 °C): $\delta = 38$, ^{31}P-NMR ([d_{10}]-DME, 25 °C): $\delta = -137.4$.

5.9. 2,5-Bis(trimethylsilyl)-1,1-dimethyl-2-(2′,3′,5′,6′-tetramethylphenyl)-4-{[(2′,3′,5′,6′-tetramethylphenyl)dimethylamino]boryl}-(deloc-2,3,5)-1-azonium-2,5-diborolane-3-ide (5a)

1.06 g (10.6 mmol) bis(dimethylamino)borane were added to a solution of 3.38 g (7.34 mmol) of compound **6** in 150 ml pentane at −30 °C. After warming to r.t. and 16 h stirring, the volume was reduced to 10 ml and cooled to −30 °C yielding colourless crystals, m.p. 148 °C. Yield: 2.8 g (70%) **7b**: ^{1}H-NMR (500 MHz, $CDCl_3$, −40 °C): $\delta = -0.22$, −0.10 (each s, each 9H, $Si(CH_3)_3$), 2.27, 2.28, 2.30, 2.32, 2.47 (each s, altogether 24H, *o*- and *m*-CH_3), 2.35, 2.76, 2.81, 3.27 (each s, each 3H, NMe_2), 6.96, 7.02 (each s, each 1H, *p*-H), ^{13}C-NMR (125 MHz, $CDCl_3$, −40 °C): $\delta = 0.2$, 0.5 (each q, each 3C, $Si(CH_3)_3$), 20.0, 20.1, 20.2, 20.4, 20.5, 20.6, 22.9 (each q, altogether 8C, *o*- and *m*-CH_3), 32.1 (br. d, 1C, B_2CH, $J = 115$ Hz), 39.2, 41.9, 44.6, 44.7 (each q, each 1C, NMe_2), 75.4 (br. s, 1C, $CSiMe_3$), 129.0, 130.3 (each d, each 1C, *p*-C), 132.2, 132.5, 132.6, 132.8, 132.9, 133.9, 136.2, 136.5 (each s, each 1C, *o*- and *m*-C), 138.4, 147.1 (each br. s, each 1C, *i*-C), ^{11}B-NMR (96 MHz, $CDCl_3$, 25 °C): $\delta = -7$, 30, 43.

5.10. 4,4-Bis(trimethylsilyl)-1-(2′,3′,5′,6′-tetramethylphenyl)-2-diethylamino-3-{[(2′,3′,5′,6′-tetramethylphenyl)dimethylamino]boryl}-3-dehydro-1,2-μH-(deloc-1,2,3)-1,2-diboretane (7b)

1.98 g (12.69 mmol) bis(diethylamino)borane were added to a solution of 5.82 g (12.69 mmol) of compound **6** in 200 ml pentane at r.t. After 7 h stirring, all volatiles were removed and the residue crystallized from *n*-hexane at −30 °C. Colourless crystals, m.p. 120 °C (dec.). Yield: 4.1g (53%) **5a**: ^{1}H-NMR (500 MHz, $CDCl_3$, −10 °C): $\delta = -0.47$, 0.07 (each s, each 9H, $Si(CH_3)_3$), 0.95, 0.96, 1.19, 1.22 (each t, each 3H, NCH_2CH_3) 2.21, 2.23, 2.24, 2.27, 2.29, 2.39, 2.40, 2.54 (each s, altogether 24H, *o*- and *m*-CH_3), 2.95–3.10, 3.16–3.26, 3.82–3.87, 4.06–4.10 (each m, altogether 8H, NCH_2Me), 3.25 (s, 1H, BHB), 6.94, 6.97 (each s, each 1H, *p*-H), ^{13}C-NMR (125 MHz, $CDCl_3$, −10 °C): $\delta = 2.4$, 3.2 (each q, each 3C, $Si(CH_3)_3$), 13.6, 13.7, 14.5, 15.1 (each q, each 1C, NCH_2CH_3), 14.8 (br. s, 1C, CSi_2), 20.0, 20.2, 20.6, 20.7, 20.7, 20.8, 22.8 (each q, altogether 8C, *o*- and *m*-CH_3), 35.8 (br. s, 1C, B_2C), 39.7, 41.1, 42.3, 45.5 (each t, each 1C, NCH_2Me), 129.7, 130.5 (each d, each 1C, *p*-C), 132.2, 132.7, 132.9, 134.2, 135.2, 137.1, 139.4 (each s, each 1C, *o*- and *m*-C), 135.9, 147.3 (each br. s, each 1C, *i*-C), ^{11}B-NMR (96 MHz, $CDCl_3$, 25 °C): $\delta = -6$, 38 (2B).

*5.11. Generation of the trishomoaromatic trans-2,5-bis(trimethylsilyl)-2,6-bis(2′,3′,5′,6′-tetramethylphenyl)-4-trimethylsilylmethyl-1-oxa-2,4,6-triboracyclohexane-(deloc-2,4,6)-dianion (**12a**)*

6.6 mmol lithiumnaphtalinide (0.44 ml of a 1.57 molar THF solution) was added to a precooled (−78 °C) solution of 0.19 g (3.3 mmol) *trans*-**13a** in 15 ml Et_2O. The progress of the reaction was monitored by ^{11}B-NMR spectroscopy at −60 °C. After 0.5 h the broad peaks at 73 and 51 ppm of **13a** were replaced by three sharp peaks at −12, −15 and −24 ppm (intensity ratio 1:1:1) for **12a**. These signals disappeared rapidly upon warming to −40 °C.

*5.12. trans-2,5-Bis(trimethylsilyl)methyl-2,6-bis(2′,3′,5′,6′-tetramethylphenyl)-4-trimethylsilylmethyl-1-oxa-2,4,6-triboracyclohexane (**13a**)*

3.7 ml (10 mmol) of HCl in Et_2O were added dropwise to a suspension of 3.0 g (5.11 mmol) of **14a**$\cdot Li_2 \cdot (Et_2O)_3$ in 30 ml Et_2O precooled to −50 °C. After 3 h stirring, the solvent was removed under high vacuum at −10 °C, the residue digested with ca. 20 ml pentane, LiCl separated by a D3 reversed frit and washed two times with 10 ml pentane. The combined filtrates were concentrated under high vacuum and cooled to −35 °C. Colourless crystals, yield 1.90 g (65%). *trans*-**13a**: ^1H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.00$ (s, 18H, $(SiMe_3)_2$), 0.19 (s, 9H, $SiMe_3$), 0.83, 1.24 (each d, each 1H, CH_2, $^1J(HH) = 12.0$ Hz), 2.21, 2.32 (each s, each 12H, *o*- and *m*-CH_3), 2.42 (s, 2H, B_2CH), 6.96 (s, 2H, *p*-H), ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 2.5$ (3C, $SiMe_3$), 2.6 (6C, $SiMe_3$) 20.2, 20.6 (each 4C, *o*- and *m*-CH_3), 22.8 (1C, CH_2), 47.2 (br., 2C, B_2CH, $^1J(CH) = 103$ Hz), 132.3, 133.5, 136.6 (10C, *o*-, *m*- a. *p*-C), 141.0 (br., 2C, *i*-C), ^{11}B-NMR (96 MHz, $CDCl_3$, 25 °C): $\delta = 73$, 51(2B).

*5.13. 2,5-Bis(trimethylsilyl)methyl-2,6-bis(2′,3′,5′,6′-tetramethylphenyl)-4-trimethylsilylmethyl-1-oxa-2,4,6-triboracyclohexane-3,5-diide (**14a**)*

0.2 g (28.8 mmol) Li dust were added to a stirred solution of 4.0 g (6.98 mmol) **15a** in 60 ml Et_2O. The progress of the reaction was monitored by ^{11}B-NMR-spectroscopy. After 2 h the signals of **15a** at 72 and 57 ppm disappeared and two new peaks at 62 and 42 ppm appeared. Excess Li was separated by a D3 reversed frit, the volume of solvent reduced to 10 ml and the solution cooled to −35 °C. Colourless crystals, yield 0.79 g (20%). **14a**$\cdot Li_2 \cdot (Et_2O)_3$: ^1H-NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 0.43$ (s, 18H, $SiMe_3$), 0.64 (s, 9H, $SiMe_3$), 1.58 (s, 2H, CH_2), 2.10, 2.12, 2.33, 2.58 (each s, each 6H, *o*- and *m*-CH_3), 6.77 (s, 2H, *p*-H), ^{13}C-NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 3.3$ (3C, $SiMe_3$), 6.0 (6C, $SiMe_3$), 18.0 (br., 1C, CH_2B), 19.4, 20.1, 21.1, 21.7 (each 2C, *o*- and *m*-CH_3), 130.3, 132.6, 132.9, 134.2, 136.4 (10C, *o*-, *m*- and *p*-C), 150.0 (br., 2C, *i*-C), the signal for the skeletal carbon atoms could not be observed under these conditions. ^{11}B-NMR (96 MHz, Et_2O, 25 °C): $\delta = 42$, 61.

*5.14. 2,5-Bis(trimethylsilyl)methyl-2,6-bis(2′,3′,5′,6′-tetramethylphenyl)-4-trimethylsilylmethyl-1-oxa-2,4,6-triborabicyclo[3.1.0]hexane (**15a**)*

5.3 ml (4.45 mmol) of Me_3SiCH_2Li (0.84 M Et_2O solution) were added to a solution of 2.32 g (4.45 mmol) of compound **15b** in 50 ml pentane dropwise. After stirring over night, all volatiles were removed under high vacuum. The residue was digested with 20 ml pentane, LiCl separated by a reversed frit, washed two times with 10 ml pentane. The volume of the combined filtrates was reduced to 10 ml and cooled to −35 °C. Colourless crystals. Yield: 1.67 g (72%). **15a**: ^1H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.11$ (s, 18H, $SiMe_3$), 0.23 (s, 9H, $SiMe_3$) 1.48 (s, 2H, CH_2), 2.17, 2.19, 2.30 (each s, altogether 24H, *o*- and *m*-CH_3), 6.92 (s, 2H, *p*-H), ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 1.8$ (3C, $SiMe_3$), 2.1 (6C, $SiMe_3$), 13.9 (br., 1C, CH_2B), 19.4, 19.5, 20.4, 21.2 (each 2C, *o*- and *m*-CH_3), 46.7 (br., 2C, $C_{3,5}$) 131.3, 132.6, 133.8, 134.4 (10C, *o*-, *m*- a. *p*-C), 140.3 (br., 2C, *i*-C), ^{11}B-NMR (96 MHz, $CDCl_3$, 25 °C): $\delta = 72$, 59 (2B).

*5.15. X-ray structure determinations of **2a**, **2c**, **2d**$\cdot Et_2O$, **5a**, **7b**$\cdot 0.5C_6H_{14}$, **13b**, **14a**$\cdot Li_2 \cdot (Et_2O)_3$*

Crystal data and details of the structure determinations are listed in Tables 2 and 3. The structures were solved by direct methods (SHELXS-86 or -97) [27] and refined by least-squares methods based on F^2 against all measured reflections (SHELXL-97 and SHELXTL NT5.1) [27]. For **2a** and **2c** a semiempirical absorption correction based on equivalent reflections was applied. All non-hydrogen atoms were refined using anisotropic displacement parameters. The structure of **2d**$\cdot Et_2O$ shows two geometrically very similar independent molecules and two ether molecules in the asymmetric unit, the listed bond lengths and angles are average values. In **7b**$\cdot 0.5C_6H_{14}$ one of the NEt_2 groups is disordered, the *n*-hexane solvent molecule is placed on an inversion center and shows disorder or dynamical behaviour as well. **14a**$\cdot Li_2 \cdot (Et_2O)_3$ crystallized as a (1 0 0) reflection twin. With a monoclinic angle close to 90° the structure could be refined as pseudomerohedral twin (refined twin ratio 28.2(1)%). The very large asymmetric unit contains two independent moieties, differing mainly in the orientation of the ether molecules coordinated to the Li atoms. The geometrical parameters are listed for the first unit only because the second one shows disorder of the ether ethyl residues.

Table 3
Crystallographic and experimental data for **2a**, **2c**, **2d**·Et_2O, **5a**, **7b**·$0.5C_6H_{14}$, **13b** and **14a**·Li_2·$(Et_2O)_3$

	2a	**2c**	**2d**·Et_2O	**5a**	**7b**·$0.5C_6H_{14}$	**13b**	**14a**·Li·$(Et_2O)_3$
Formula	$C_{22}H_{54}B_4Cl_1N_3Si_2$	$C_{18}H_{47}B_2Cl_1P_2Si_4$	$C_{44}H_{65}B_2OPSi_2$	$C_{32}H_{57}B_3N_2Si_2$	$C_{39}H_{72}B_3N_2Si_2$	$C_{32}H_{57}B_3OSi_3$	$C_{44}H_{85}B_3Li_2O_4Si_3$
Formula weight (g mol^{-1})	495.55	494.93	718.73	558.41	657.60	574.48	808.70
Colour, habit	Colourless, irregular	Colourless, prism	Colourless platelet	Colourless, block	Colourless, octahedral	Colourless, irregular	Colourless, irregular, (100) twin
Crystal size (mm^3)	0.56 × 0.48 × 0.40	0.25 × 0.25 × 0.10	0.55 × 0.35 × 0.05	0.40 × 0.30 × 0.30	0.50 × 0.25 × 0.25	0.65 × 0.50 × 0.45	0.48 × 0.33 × 0.24
Crystal system	Triclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	*Ia* (No. 9)
a (Å)	10.0555(3)	16.323(1)	15.342(1)	9.080(1)	9.639(1)	11.724(1)	17.415(1)
b (Å)	10.8553(3)	12.3956(8)	18.647(2)	11.338(1)	20.352(2)	12.194(1)	18.202(1)
c (Å)	16.2028(4)	30.922(2)	18.714(1)	18.745(1)	21.574(2)	13.500(1)	33.547(2)
α (°)	106.395(2)		69.26(1)	77.46(1)		94.31(1)	
β (°)	92.056(3)		67.69(l)	82.68(l)	97.49(1)	93.82(1)	90.53(1)
γ (°)	113.043(2)		68.96(1)	72.99(1)		107.87(1)	
V (Å^3)	1539.72(7)	6256.7(7)	4473.2(6)	1797.1(3)	4196.1(5)	1823.5(3)	10 634(1)
Z	2	8	4	2	4	2	8
Calculated density (Mg m$-^{3}$)	1.069	1.051	1.067	1.032	1.041	1.046	1.010
Absorption μ (mm^{-1})	0.217	0.382	0.145	0.120	0.112	0.152	0.123
Temperature (K)	173(1)	173(1)	193(1)	190(1)	193(1)	193(1)	193(1)
λ(Mo–K_α) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Diffractometer	SMART (Bruker)	SMART (Bruker)	IPDS (Stoe)	IPDS (Stoe)	IPDS (Stoe)	IPDS (Stoe)	IPDS (Stoe)
θ max (°)	28.3	26.4	24.1	25.9	26.0	25.9	24.0
Reflections: total, unique, observed [$> 4\sigma(F)$]	20 361, 7454, 5847	38 585, 6408, 4629	36 494, 13 386, 6423	14 965, 6503, 3675	32 795, 8152, 5221	18 093, 6620, 4926	39 454, 16 332, 9463
No. of parameters	505	432	938	374	444	385	1019
R ($F > 4\sigma(F)$)	0.0387	0.0393	0.0475	0.0362	0.0420	0.0404	0.0550
wR_2 (all reflections)	0.1078	0.1016	0.1111	0.0847	0.1085	0.1076	0.1252
GOF, S	1.029	1.039	0.799	0.821	0.918	0.938	0.880
Residual density (e Å$-^{3}$)	0.53, −0.35	0.35, −0.32	0.62, −0.29	0.17, −0.18	0.23, −0.30	0.32, −0.19	0.52, −0.23

Due to the twinning and disorder problems, the precision of geometrical parameters is reduced for this structure.

6. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC-204528 (**2a**), CCDC-204529 (**2c**), CCDC-204530 (**2d**·Et_2O), CCDC-204531 (**5a**), CCDC-204532 (**7b**·$0.5C_6H_{14}$), CCDC-204533 (**13b**), CCDC-204534 (**14a**·Li_2·$(Et_2O)_3$). Copies of the data can be obtained free of charge and by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 247 and FSP Polyeder), the Fonds der Chemischen Industrie, the University of Georgia, and National Science Foundation Grant CHE-0209857.

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